Practical guide to OpenMX calculations

- Getting started with a cif file
- Benchmark calculations by runtest(L)
- Specification of PAO and VPS
- Choice of the cutoff energy
- Calculation of energy curves
- SCF calculations
- Geometry optimizations
- Choice of basis functions
- Surface states and floating states
- Restarting of the calculation
- Outputting files in a binary mode

Benchmark calculations by runtest(L)

Even after successfully completing the OpenMX installation, the program may not work properly. This problem is often caused by compiler options (-O3) or numerical libraries.

By running ‘runtest’ or ‘runtestL’, you can confirm that the whole set of functionality is working properly.

For the MPI parallel running

```
% mpirun -np 8 openmx -runtest
```

For the OpenMP/MPI parallel running

```
% mpirun -np 8 openmx -runtest -nt 2
```

The results are output to ‘runtest.result’ showing the difference between the stored results (total energy and force).

1	input_example/Benzene.dat	Elapsed time(s)= 4.78	diff Utot= 0.000000000000	diff Force= 0.000000000002
2	input_example/C60.dat	Elapsed time(s)= 14.96	diff Utot= 0.000000000019	diff Force= 0.000000000004
3	input_example/CO.dat	Elapsed time(s)= 9.86	diff Utot= 0.000000000416	diff Force= 0.000000000490
4	input_example/Cr2.dat	Elapsed time(s)= 10.70	diff Utot= 0.000000000000	diff Force= 0.000000000044
5	input_example/Crys-MnO.dat	Elapsed time(s)= 19.98	diff Utot= 0.000000004126	diff Force= 0.000000001888
6	input_example/GaAs.dat	Elapsed time(s)= 26.39	diff Utot= 0.000000001030	diff Force= 0.000000000007
7	input_example/Glycine.dat	Elapsed time(s)= 5.48	diff Utot= 0.000000000001	diff Force= 0.000000000000
8	input_example/Graphite4.dat	Elapsed time(s)= 5.00	diff Utot= 0.000000002617	diff Force= 0.000000015163
9	input_example/H2O-EF.dat	Elapsed time(s)= 4.88	diff Utot= 0.000000000000	diff Force= 0.000000000113
10	input_example/H2O.dat	Elapsed time(s)= 4.60	diff Utot= 0.000000000008	diff Force= 0.000000013375
11	input_example/HMn.dat	Elapsed time(s)= 13.44	diff Utot= 0.000000000001	diff Force= 0.000000000001
12	input_example/Methane.dat	Elapsed time(s)= 3.64	diff Utot= 0.000000000001	diff Force= 0.000000002263
13	input_example/Mol_MnO.dat	Elapsed time(s)= 9.43	diff Utot= 0.000000003714	diff Force= 0.000000000540
14	input_example/Ndia2.dat	Elapsed time(s)= 5.67	diff Utot= 0.000000000004	diff Force= 0.000000000001

Total elapsed time (s) 138.79

‘runtestL’ is a test with a large job. It is useful for measuring machine performance.
Results on various computers are available in work/input_example and work/large_example.

Database of PAO and VPS

https://t-ozaki.issp.u-tokyo.ac.jp/vps_pao2019/

Database (2019) of optimized VPS and PAO

The database (2019) of fully relativistic pseudopotentials (VPS) and pseudo-atomic orbitals (PAO), generated by ADPACK, which could be an input data of program package, OpenMX. The data of elements with the underline are currently available. When you use these data, VPS and PAO, in the program package, OpenMX, then copy them to the directory, openmx*.*/DFT_DATA19/VPS/ and openmx*.*/DFT_DATA19/PAO/, respectively. The delta gauge of OpenMX with the database (2019) is found at here.

Public release of optimized and well tested VPS and PAO so that users can easily start their calculations.

E																	
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	L	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	A															
	L	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
	A	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Specification of PAO and VPS

PAO and VPS are specified by the following keyword:

```
<Definition.of.Atomic.Species
  O    O7.0-s2p2d1       O_PBE19
  H    H7.0-s2p1         H_PBE19
Definition.of.Atomic.Species>
```

- O7.0 means O7.0.pao.
- -s2p2d1 means 2, 2, and 1 radial functions are allocated to s-, p-, and d-orbitals.
- In this case, for oxygen atom, 2×1+2×3+1×5=13 basis functions are allocated.
- O_PBE19 means O_PBE19.vps.

The path for O7.0.pao and O_PBE13.vps is specified by

DATA.PATH ../DFT_DATA19

Default value is '../DFT_DATA19'.

How to choose basis functions: H_2O case

By clicking H7.0.pao and O7.0.pao in the database(2019), you may find the following

https://t-ozaki.issp.u-tokyo.ac.jp/vps_pao2019/H/index.html

H7.0.pao

```
**************************************************
  Eigen values(Hartree) of pseudo atomic orbitals
**************************************************

Eigenvalues
Lmax= 3 Mul=15
  | mu    0  0     -0.23595211038442   <- 3
  | mu    0  1      0.14109389991827   <- 6
  | mu    0  2      0.61751730037441
  | mu    0  3      1.31890671598573
  | mu    0  4      2.24052765608302
  | mu    0  5      3.37954791544661
  | mu    0  6      4.73488369825610
  | mu    0  7      6.30608874470710
  | mu    0  8      8.09282718517299
  | mu    0  9     10.09464035732420
  | mu    0 10     12.31085267019158
  | mu    0 11     14.74057314485273
  | mu    0 12     17.38277845742691
  | mu    0 13     20.23645090753857
  | mu    0 14     23.30073926597344   <- 5
  | mu    1  0      0.10914684890465
  | mu    1  1      0.47776040452236
  | mu    1  2      1.06988680483686
  | mu    1  3      1.88261331124981
  | mu    1  4      2.91175885838084
  | mu    1  5      4.15601184789448
  | mu    1  6      5.61454131060210
  | mu    1  7      7.28681796296307
  | mu    1  8      9.17254361476158
  | mu    1  9     11.27156766390586
  | mu    1 10     13.58381334569800
  | mu    1 11     16.10921637499960
  | mu    1 12     18.84767560575107
  | mu    1 13     21.79902110024685
  | mu    1 14     24.96300480798286
  | mu    2  0      0.27851528500170
  | mu    2  1      0.76970400958463
  | mu    2  2      1.47576814497054
  | mu    2  3      2.39881523735167
  | mu    2  4      3.53713346447754
```

https://t-ozaki.issp.u-tokyo.ac.jp/vps_pao2019/O/index.html

O7.0.pao

```
**************************************************
  Eigen values(Hartree) of pseudo atomic orbitals
**************************************************

Eigenvalues
Lmax= 3 Mul=15
  | mu    0  0     -0.87913976280231   <- 1
  | mu    0  1      0.06809061901229   <- 4
  | mu    0  2      0.52709275865941
  | mu    0  3      1.24995140722317
  | mu    0  4      2.21829552402723
  | mu    0  5      3.41945468859267
  | mu    0  6      4.84509607059749
  | mu    0  7      6.48825090142865
  | mu    0  8      8.34207134316001
  | mu    0  9     10.39973244132192
  | mu    0 10     12.65513764955926
  | mu    0 11     15.10428688136984
  | mu    0 12     17.74677530362947
  | mu    0 13     20.58633940582683
  | mu    0 14     23.62957122674031   <- 2
  | mu    1  0     -0.33075182895384
  | mu    1  1      0.16376499567753   <- 7
  | mu    1  2      0.64129274864838
  | mu    1  3      1.35995471521821
  | mu    1  4      2.31377697411480
  | mu    1  5      3.50052618379026
  | mu    1  6      4.91841590421346
  | mu    1  7      6.56499793348396
  | mu    1  8      8.43634105410091
  | mu    1  9     10.52733540479795
  | mu    1 10     12.83276989780839
  | mu    1 11     15.34880171573570
  | mu    1 12     18.07414632417004
  | mu    1 13     21.01013110934429
  | mu    1 14     24.15933607166566   <- 8
  | mu    2  0      0.26162948257116
  | mu    2  1      0.70705247436937
  | mu    2  2      1.34714706672243
  | mu    2  3      2.19799459356269
  | mu    2  4      3.26511989658328
```

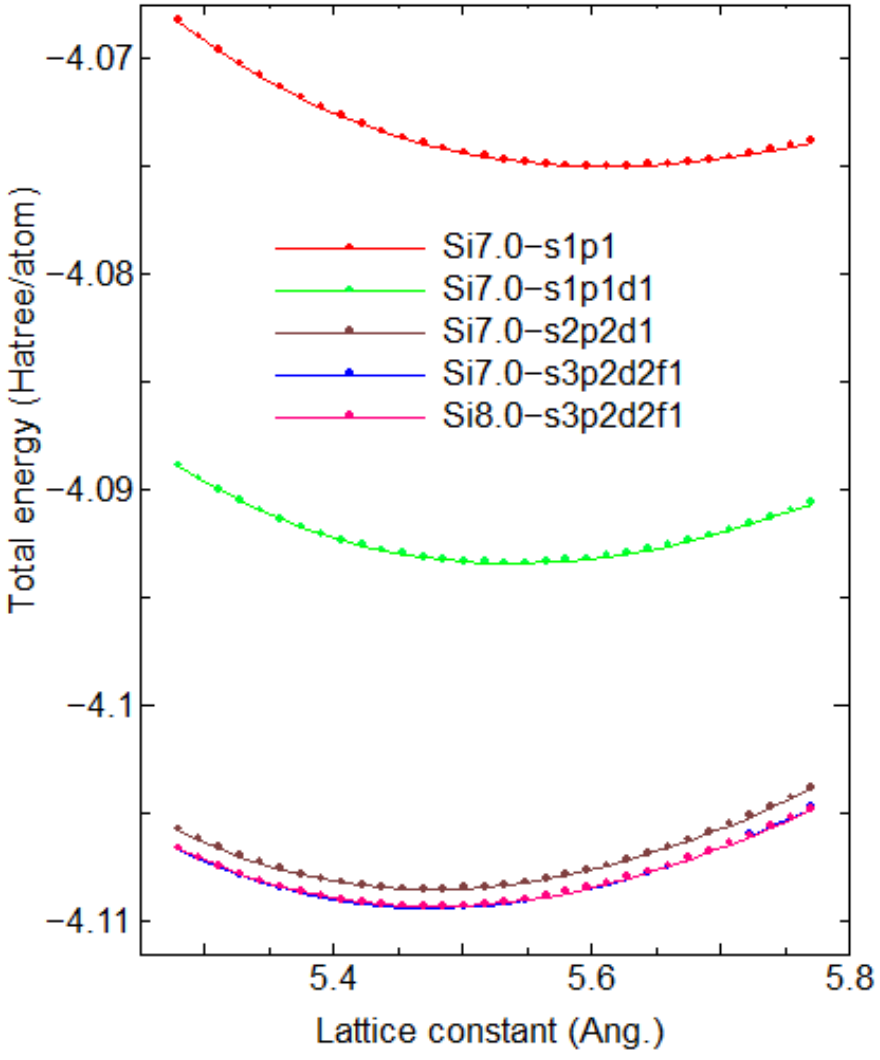
Choosing states with lower eigenvalues leads to H7.0-s2p1 and O7.0-s2p2d1.

How to choose basis functions: Si case(1)

Si7.0.pao

```
Eigenvalues
Lmax= 3 Mul=15
 | mu    0  0     -0.59320968623145 1
 | mu    0  1      0.01654247265872 4
 | mu    0  2      0.57915688461708 8
 | mu    0  3      1.39915528592998
 | mu    0  4      2.43106703909053
 | mu    0  5      3.63498884739274
 | mu    0  6      4.99885012002783
 | mu    0  7      6.55485759476897
 | mu    0  8      8.33541526908920
 | mu    0  9     10.34055461939939
 | mu    0 10     12.55818051232040
 | mu    0 11     14.98369777887096
 | mu    0 12     17.62014479571136
 | mu    0 13     20.47011746372617
 | mu    0 14     23.53245309073866
 | mu    1  0     -0.31460013133101 2
 | mu    1  1      0.12937640798489 5
 | mu    1  2      0.71637380083701
 | mu    1  3      1.54488697995006
 | mu    1  4      2.59211686526084
 | mu    1  5      3.84687324239366
 | mu    1  6      5.31246180826158
 | mu    1  7      6.99509799702661
 | mu    1  8      8.89454075291723
 | mu    1  9     11.00602102880752
 | mu    1 10     13.32692005826443
 | mu    1 11     15.85857455673626
 | mu    1 12     18.60272353142246
 | mu    1 13     21.55894843635971
 | mu    1 14     24.72602323954447
 | mu    2  0      0.01886411574821 3
 | mu    2  1      0.35893514996065 7
 | mu    2  2      0.94629918754692
 | mu    2  3      1.76201765644983
 | mu    2  4      2.81418723624388
 | mu    2  5      4.10656012645961
 | mu    2  6      5.63661971875011
 | mu    2  7      7.39522693820483
 | mu    2  8      9.37222098331867
 | mu    2  9     11.56227937764802
 | mu    2 10     13.96620568880690
 | mu    2 11     16.58651812641581
 | mu    2 12     19.42296574188659
 | mu    2 13     22.47308081363278
 | mu    2 14     25.73538272482773
 | mu    3  0      0.28356769151846 6
 | mu    3  1      0.79082836114569
 | mu    3  2      1.52992065308726
 | mu    3  3      2.52537261496132
```

Orbitals with lower eigenvalues in Si7.0.pao are taken into account step by step as the quality of basis set is improved.

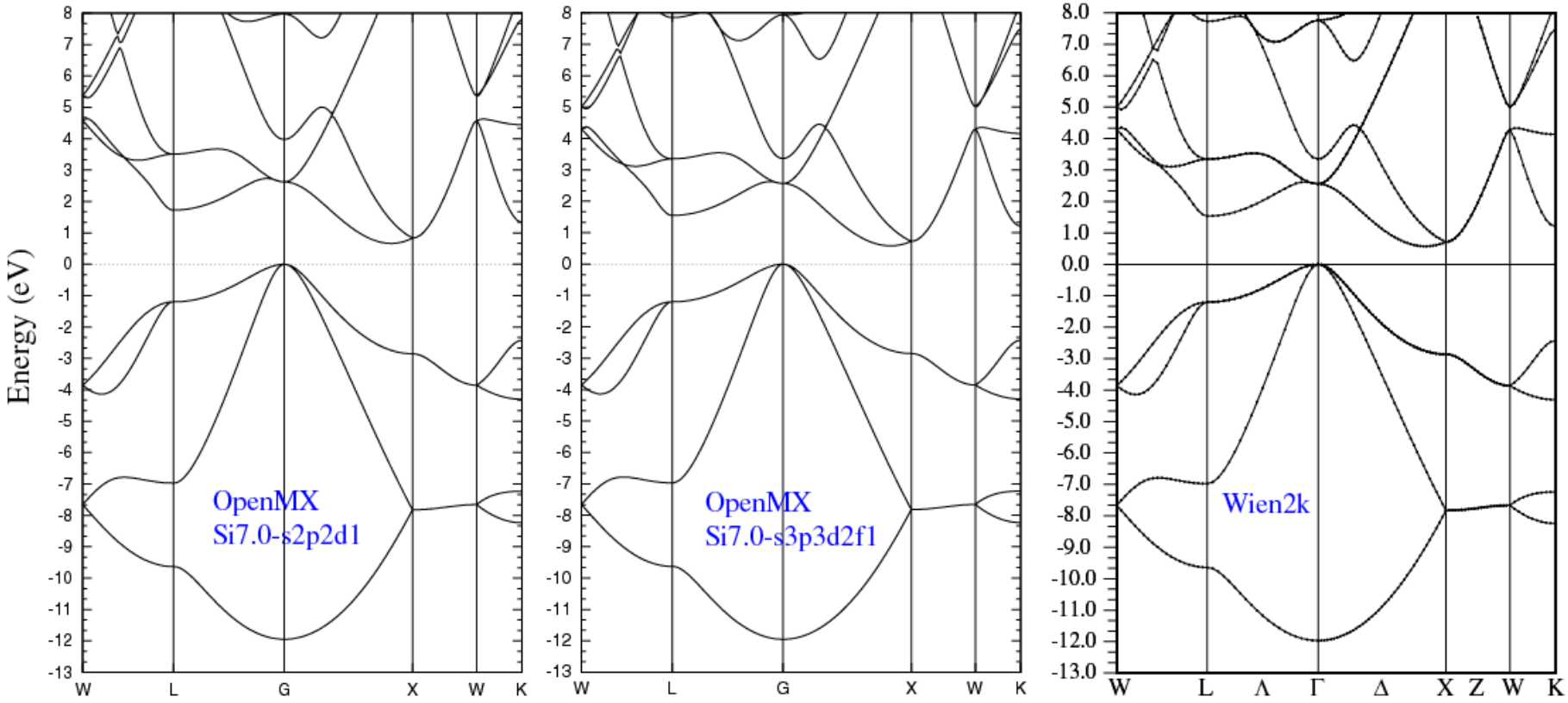


Si7.0-s2p2d1 is enough to discuss structural properties.

By comparing Si7.0-s3p2d2f1 with Si8.0-s3p2d2f1, it turns out that convergence is achieved at the cutoff of 7.0(a.u.).

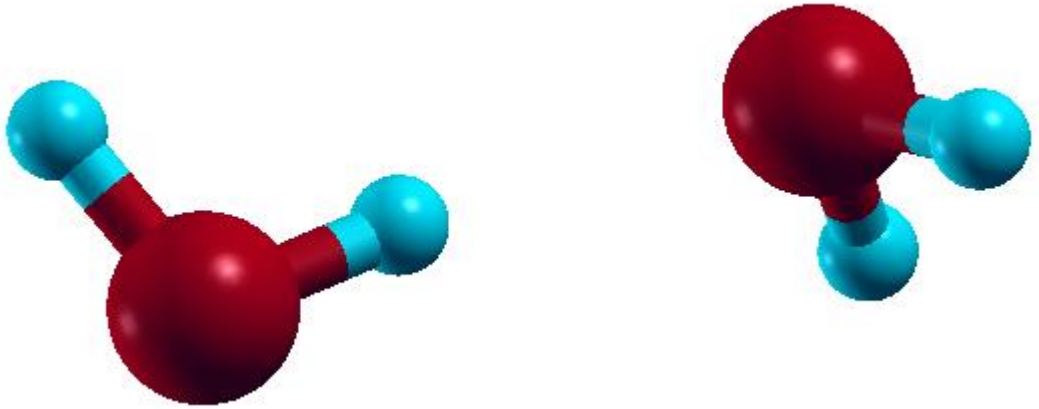
How to choose basis functions: Si case(2)

With respect to band structure, one can confirm that Si7.0-s2p2d1 provides a nearly convent result.



While the convergent result is achieved by use of Si7.0-s3p2d2f1(Si7.0-s3p3d2f1), Si7.0-s2p2d1 is a balanced basis functions compromising accuracy and efficiency to perform a vast range of materials exploration.

Basis set superposition Error (BSSE)



	Equilibrium O-O distance (Ang.)	Dipole moment (Debye)	Binding energy (kcal/mol)	Binding energy (couterpoise corrected) (kcal/mol)
O7.0-s2p2d1, H7.0-s2p1	2.899	2.54	5.57	5.21
O7.0-s3p3d2, H7.0-s3p2	2.897	2.45	5.48	5.48
Other calc.	2.893[a]		5.15 [a]	
Expt.	2.98[b]	2.60[b]	5.44 [b]	

https://t-ozaki.issp.u-tokyo.ac.jp/vps_pao2019/O/index.html

A series of benchmark calculations implies that BSSE is ～0.5 kcal/mol for molecular systems.

Recommendation of choices for PAO

VPS	Valence electrons	Quick	Standard	Precise
E	0.0	Kr10.0-s1p1	Kr10.0-s2p1d1	Kr10.0-s2p2d1f1
H_PBE19	1.0	H5.0-s2	H6.0-s2p1	H7.0-s2p2d1
He_PBE19	2.0	He8.0-s1p1	He8.0-s2p1	He10.0-s2p2d1
Li_PBE19	3.0	Li8.0-s3p1	Li8.0-s3p2	Li8.0-s3p2d1
Be_PBE19	2.0	Be7.0-s2p1	Be7.0-s2p2	Be7.0-s3p2d1
B_PBE19	3.0	B7.0-s2p2	B7.0-s2p2d1	B7.0-s3p2d2
C_PBE19	4.0	C6.0-s2p2	C6.0-s2p2d1	C6.0-s3p2d2
N_PBE19	5.0	N6.0-s2p2	N6.0-s2p2d1	N6.0-s3p2d2
O_PBE19	6.0	O6.0-s2p2	O6.0-s2p2d1	O6.0-s3p2d2
F_PBE19	7.0	F6.0-s2p2	F6.0-s2p2d1	F6.0-s3p3d2f1
Ne_PBE19	8.0	Ne9.0-s2p2	Ne9.0-s2p2d1	Ne9.0-s3p2d2
Na_PBE19	9.0	Na9.0-s3p2	Na9.0-s3p2d1	Na9.0-s3p2d2
Mg_PBE19	8.0	Mg9.0-s2p2	Mg9.0-s3p2d1	Mg9.0-s3p2d2
Al_PBE19	3.0	Al7.0-s2p1d1	Al7.0-s2p2d1	Al7.0-s3p2d2
Si_PBE19	4.0	Si7.0-s2p1d1	Si7.0-s2p2d1	Si7.0-s3p3d2
P_PBE19	5.0	P7.0-s2p2d1	P7.0-s2p2d1f1	P7.0-s3p2d2f1
S_PBE19	6.0	S7.0-s2p2d1	S7.0-s2p2d1f1	S7.0-s3p2d2f1
Cl_PBE19	7.0	Cl7.0-s2p2d1	Cl7.0-s2p2d1f1	Cl7.0-s3p2d2f1

See also the pages 55 and 56 in the manual.

Specification of the directory storing *.pao and *.vps

The directory *DFT_DATA* can be specified by the keyword in your input file as

DATA.PATH ../DFT_DATA19

Both the absolute and relative paths can be specified.

Choice of cutoff energy

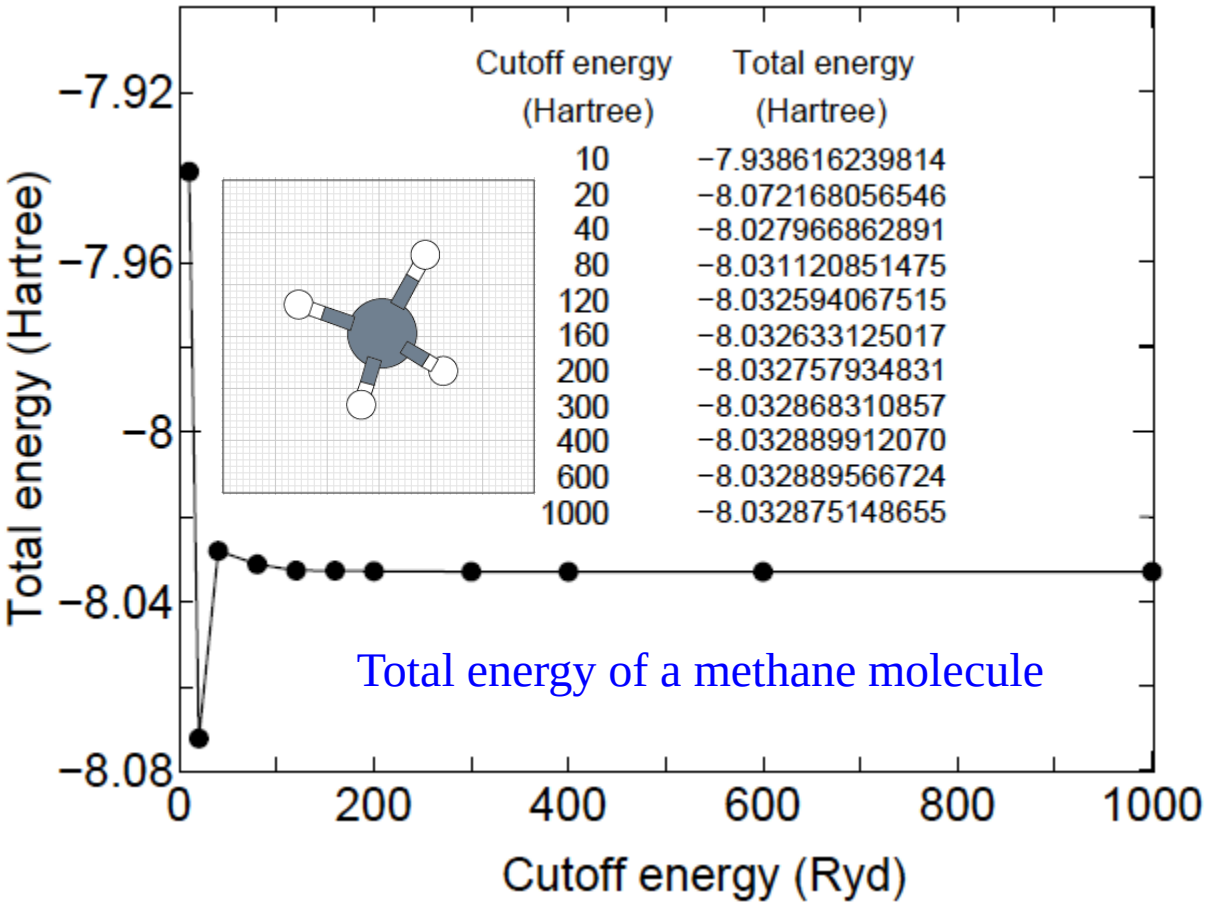
scf.energycutoff 200 # default=150 Ryd

The FFT grid is used to discretize real space and calculate $E_{\delta ee}$, E_{xc}, and can be specified by scf.energycutoff.

In most cases, 200 Ryd is enough to get convergence.

However, large cutoff energy (300-400 Ryd) has be used cases such as use of pseudopotentials with deep semi-core states.

Memory requiment
$O(E^{3/2})$



Choice of cutoff energy

Geometry optimization of H_2O

Dependency of optimized structure of H_2O on scf.energycutoff. It turns out that 180Ryd. is enough to reach the convergence.

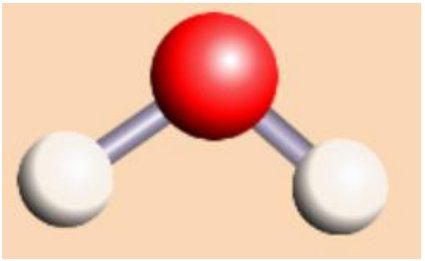


Table 1: Convergence of structural parameters, dipole moment of a water molecule with respect to the cutoff energy. The input file is 'H2O.dat' in the directory 'work'.

Ecut(Ryd)	r(H-O) (Å)	∠ (H-O-H) (deg)	Dipole moment (Debye)
60	0.970	103.4	1.838
90	0.971	103.7	1.829
120	0.971	103.7	1.832
150	0.971	103.6	1.829
180	0.971	103.6	1.833
Exp.	0.957	104.5	1.85

Volume vs. Energy curves

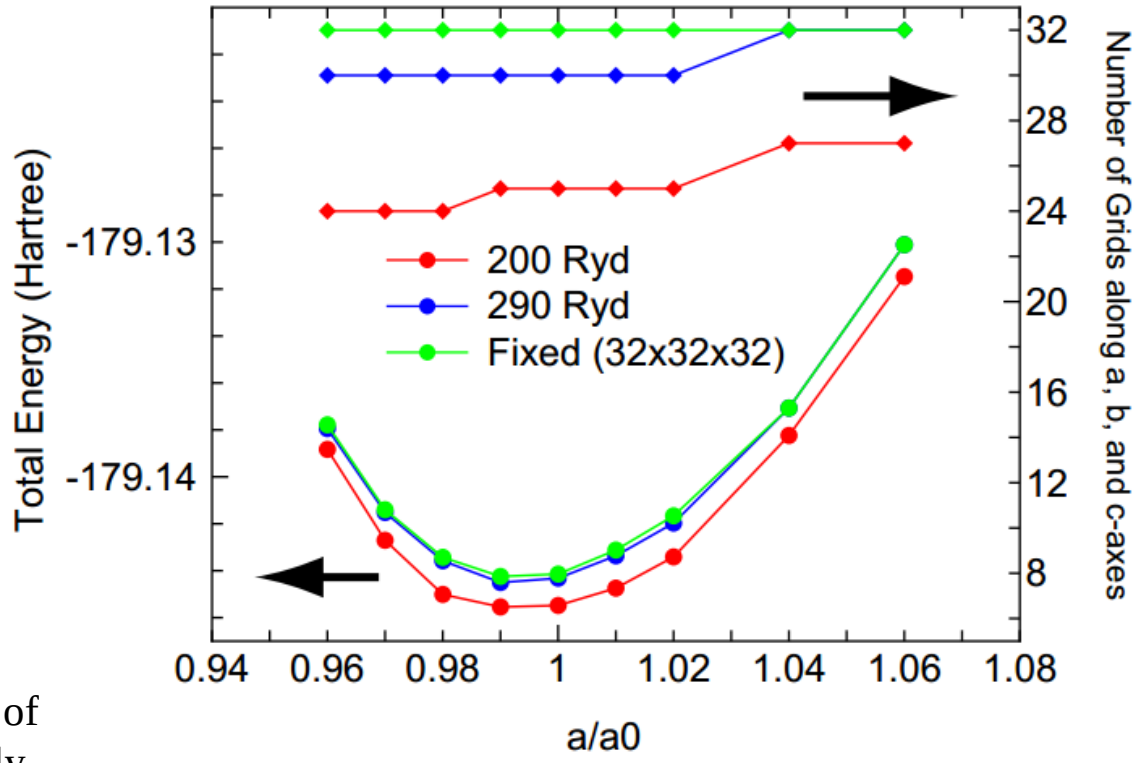
The following keywords are available to calculate energy curves.

```
MD.Type          EvsLC    #
MD.EvsLC.Step    0.4      # default=0.4%
MD.maxIter       32       # default=1
```

When the energy curve for bulk system is calculated as a function of the lattice parameter, a sudden change of the number of real space grids is a serious problem which produces an erratic discontinuity on the energy curve. To avoid this, the number of grids should be fixed by explicitly specifying the following keyword:

```
scf.Ngrid        32 32 32
```

The numbers correspond to the number of grid along a-, b-, and c-axes, respectively. scf.Ngrid is used if both the keywords scf.energycutoff and scf.Ngrid are specified.




```
MD.EvsLC.flag    1  1  0      # along a, b, c-axes
1: varied,  0: fixed
```

Self-consistency: Simple charge mixing

The KS effective is constructed from ρ.
However, ρ is evaluated from eigenfaunctions of KS eq.

$$\hat{H}_{\mathrm{KS}}\phi_i = \varepsilon_i\phi_i \qquad \hat{H}_{\mathrm{KS}} = -\frac{1}{2}\nabla^2 + v_{\mathrm{eff}}$$

$$v_{\mathrm{eff}} = v_{\mathrm{ext}}(\mathbf{r}) + v_{\mathrm{Hartree}}(\mathbf{r}) + \frac{\delta E_{\mathrm{xc}}}{\delta\rho(\mathbf{r})}$$

$$\rho(\mathbf{r}) = \sum_i \phi_i^*(\mathbf{r})\phi_i(\mathbf{r})$$

Simple charge mixing method

The next input density is constructed by a simple mixing of input and output densities.

$$\rho_{n+1}^{(\mathrm{in})} = \alpha\rho_n^{(\mathrm{in})} + (1-\alpha)\rho_n^{(\mathrm{out})},$$

It works well for large gap systems and small sized systems.

Self-consistency: RMM-DIIS

Idea:

Minimize the norm of a linear combination of previous residual vectors.

$$\bar{R}_{n+1} = \sum_{m=n-(p-1)}^{n} \alpha_m R_m,$$

$$\begin{aligned} F &= \langle \bar{R}_{n+1} | \bar{R}_{n+1} \rangle - \lambda \left(1 - \sum_m^n a_m \right), \\ &= \sum_{m,m'} \alpha_m \alpha_{m'} \langle R_m | R_{m'} \rangle - \lambda \left(1 - \sum_m^n a_m \right). \end{aligned}$$

$$R_n(\mathbf{q}) \equiv \tilde{n}_n^{(\mathrm{out})}(\mathbf{q}) - \tilde{n}_n^{(\mathrm{in})}(\mathbf{q}),$$

$$\langle R_m | R_{m'} \rangle \equiv \sum_{\mathbf{q}} \frac{R_m^*(\mathbf{q}) R_{m'}(\mathbf{q})}{w(\mathbf{q})},$$

Kerker factor

$$w(\mathbf{q}) = \frac{|\mathbf{q}|^2}{|\mathbf{q}|^2 + q_0^2},$$

Long wave length components corresponding to small |q| are taken into account.

Minimization of F leads to

$$\frac{\partial F}{\partial \alpha_k} = 0 \qquad \frac{\partial F}{\partial \lambda} = 0$$

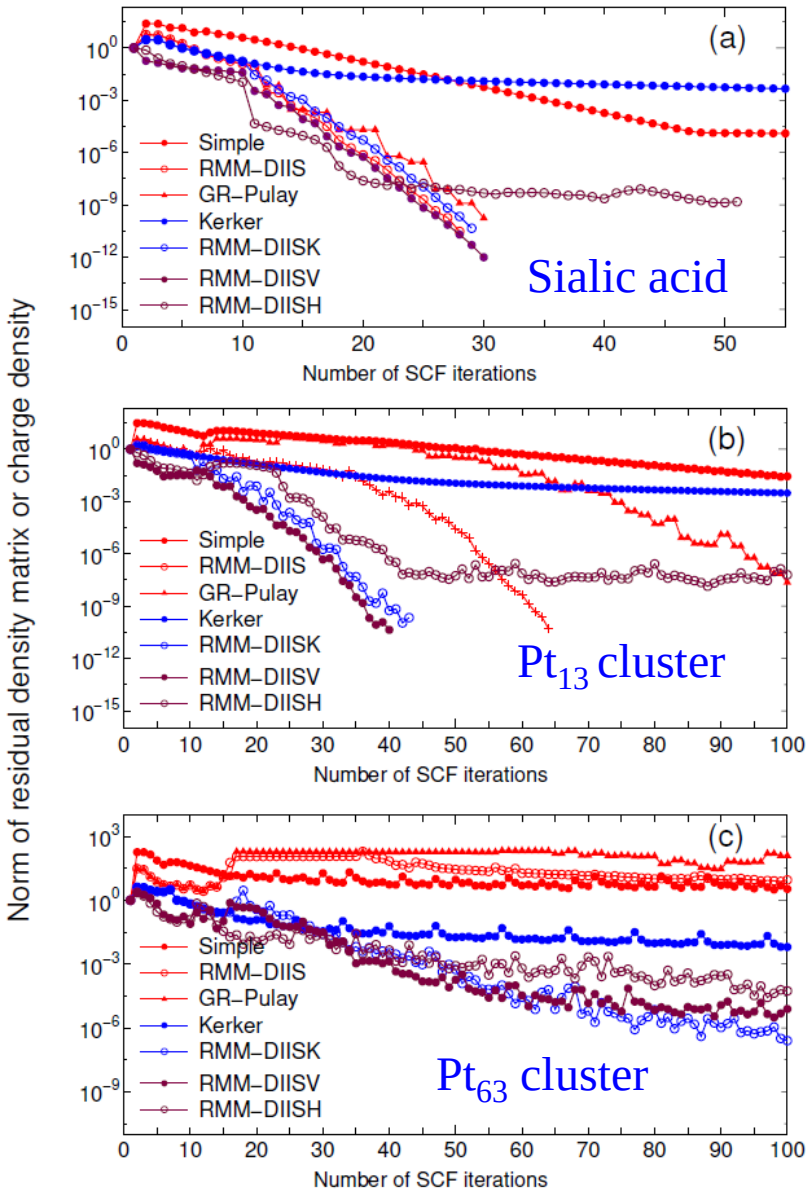
$$\begin{pmatrix} \langle R_{n-(p-1)} | R_{n-(p-1)} \rangle & \cdots & \cdots & 1 \\ \cdots & \cdots & \cdots & 1 \\ \cdots & \cdots & \langle R_n | R_n \rangle & \cdots \\ 1 & 1 & \cdots & 0 \end{pmatrix} \begin{pmatrix} \alpha_{n-(p-1)} \\ \alpha_{n-(p-1)+1} \\ \cdot \\ \frac{1}{2}\lambda \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \cdot \\ 1 \end{pmatrix}.$$

Optimum input density might be given by

$$\rho_{n+1}^{(\mathrm{in})} = \sum_{m=n-(p-1)}^{n} \alpha_m \rho_m^{(\mathrm{in})} + \beta \sum_{m=n-(p-1)}^{n} \alpha_m R_m$$

G.Kresse and J. Furthmeuller, PRB 54, 11169 (1996).

Mixing methods



Available mixing methods:

Simple mixing (Simple)

Residual minimization method in the direct inversion iterative subspace (RMM-DIIS)

Guaranteed reduction Pulay method (GR-Pulay)

Kerker mixing (Kerker)

RMM-DIIS with Kerker metric (RMM-DIISK)

RMM-DIIS for Kohn-Sham potential (RMM-DIISV)

RMM-DIIS for Hamiltonian (RMM-DIISH)

Recommendation:
RMM-DIISK or RMM-DIISV

For DFT+U and constrained methods
RMM-DIISH

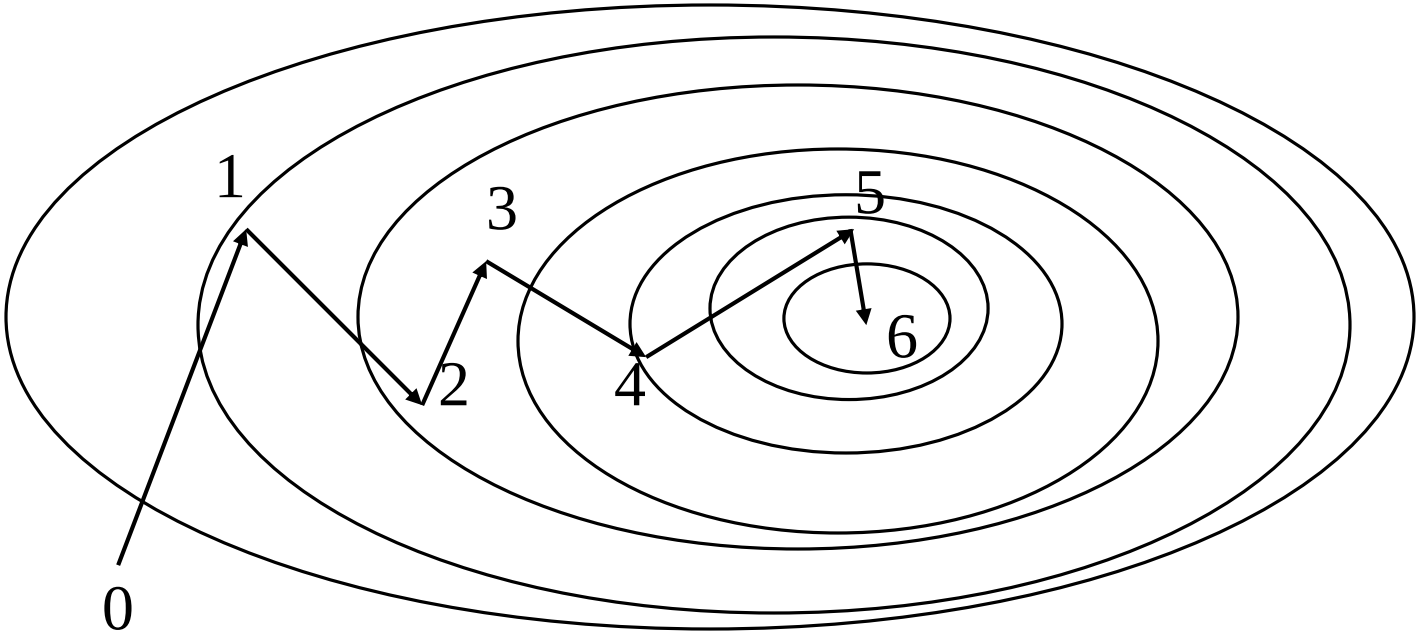
See also the page 63 in the manual.

Geometry optimization

To quantitatively investigate structural, physical, and chemical properties of molecules and solids, it would be important to obtain optimized structures.

Steepest decent (SD) method

The structure is changed along the steepest decent step by step.



It may not be so efficient.

Geometry optimization by the SD method

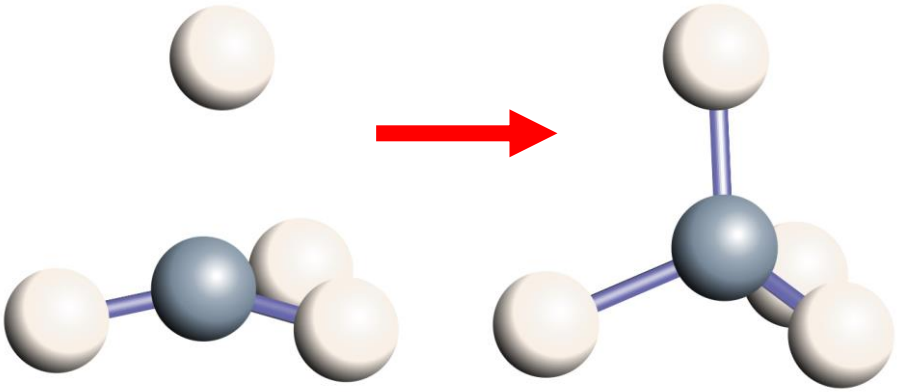
Let us change the *x*-coordinate of carbon atom in a methane molecule to 0.3 Å as

```
<Atoms.SpeciesAndCoordinates
   1   C     0.300000    0.000000    0.000000     2.0  2.0
   2   H    -0.889981   -0.629312    0.000000     0.5  0.5
   3   H     0.000000    0.629312   -0.889981     0.5  0.5
   4   H     0.000000    0.629312    0.889981     0.5  0.5
   5   H     0.889981   -0.629312    0.000000     0.5  0.5
 Atoms.SpeciesAndCoordinates>
```

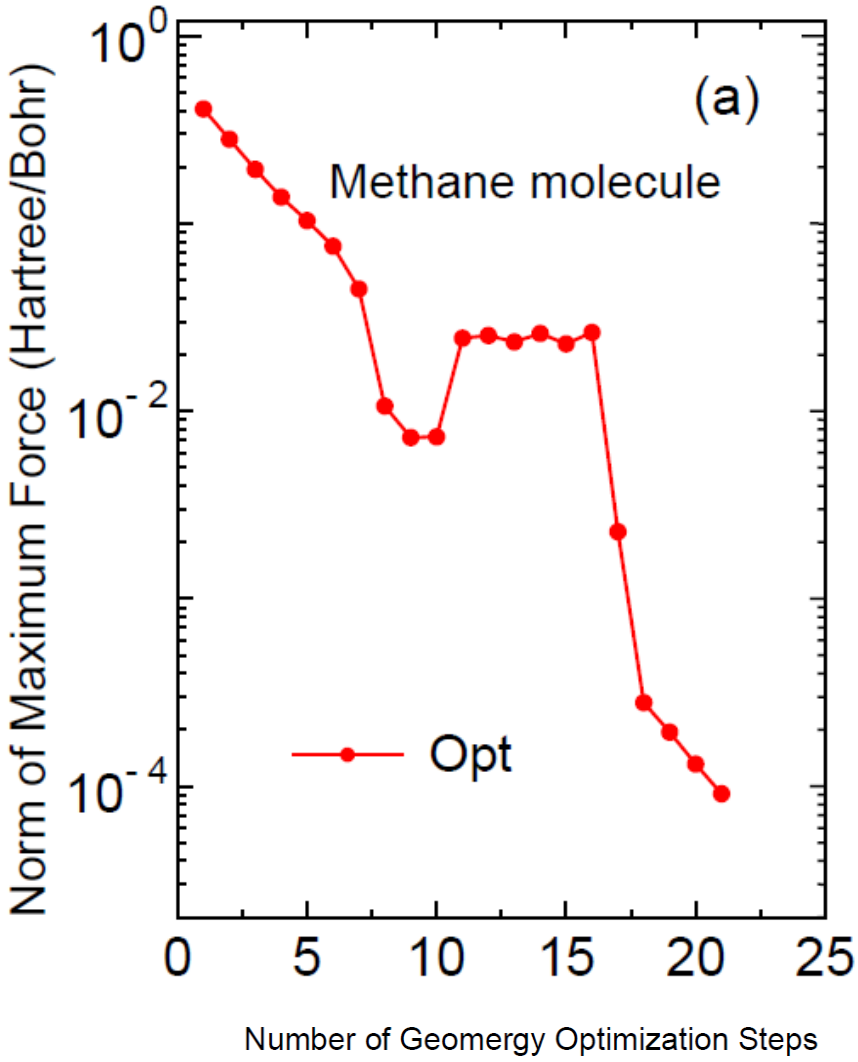
Using “Methane2.dat” in the directory “work”, you can trace the calculation.

Initial structure

Final structure



Optimization process



Relevant output files for the geometry optimization

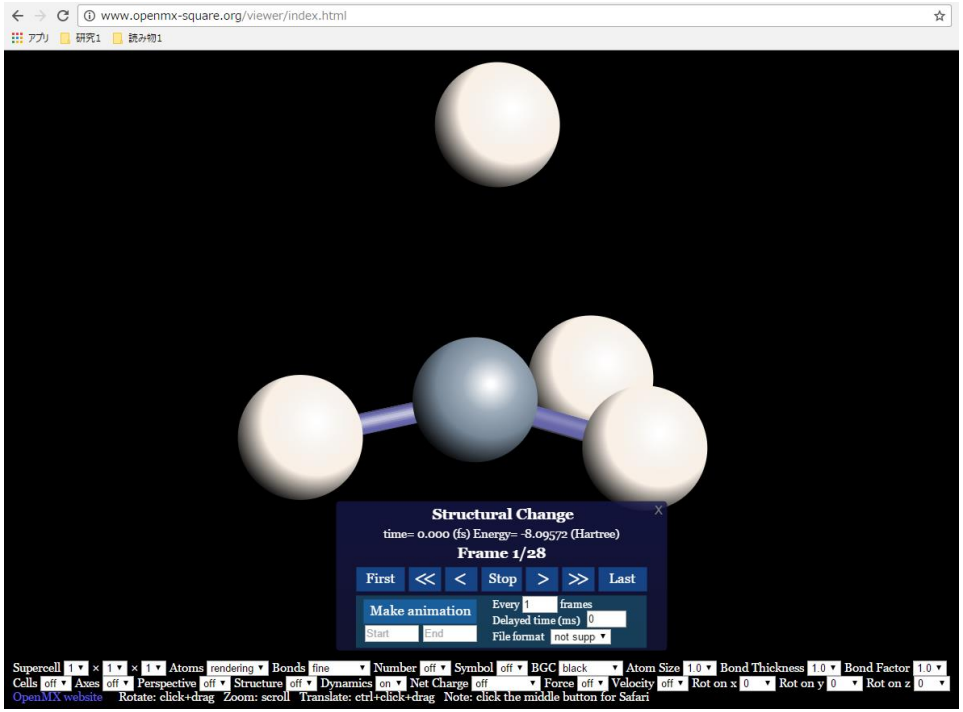
In met2.out, the history of optimization can be confirmed.

By dragging and dropping met2.md to OpenMX Viewer, the optimization process can be easily visualized.

```
************************************************************
************************************************************
             History of geometry optimization
************************************************************
************************************************************

  MD_iter    SD_scaling      |Maximum force|    Maximum step        Utot
                             (Hartree/Bohr)        (Ang)          (Hartree)

     1       1.25981733        0.40873710       0.10583545      -8.09571722
     2       1.25981733        0.12000148       0.08000099      -8.16523842
     3       1.25981733        0.06115237       0.04076824      -8.18400222
     4       1.25981733        0.01811189       0.01207460      -8.18831175
     5       3.14954331        0.01076505       0.01794175      -8.18898468
     6       3.14954331        0.00576811       0.00961351      -8.18980390
     7       3.14954331        0.00355034       0.00591724      -8.19010991
     8       3.14954331        0.00255760       0.00426266      -8.19022887
     9       7.87385828        0.00218904       0.00912099      -8.19027446
    10       7.87385828        0.00863395       0.03597478      -8.19023586
    11       1.57477166        0.04692594       0.03910495      -8.18816953
    12       1.57477166        0.01357319       0.01131099      -8.19012703
    13       3.93692914        0.00406864       0.00847634      -8.19029047
    14       3.93692914        0.00915707       0.01907723      -8.19022710
    15       0.78738583        0.02067017       0.00861257      -8.18990108
    16       0.78738583        0.00721609       0.00300671      -8.19025699
    17       1.96846457        0.00255359       0.00265999      -8.19030094
    18       1.96846457        0.00163789       0.00170613      -8.19030460
    19       1.96846457        0.00105501       0.00109897      -8.19030613
    20       1.96846457        0.00068667       0.00071528      -8.19030671
    21       4.92116143        0.00044434       0.00115713      -8.19030697
    22       4.92116143        0.00138402       0.00360421      -8.19030537
    23       0.98423229        0.00427346       0.00222576      -8.19028994
    24       0.98423229        0.00078570       0.00040922      -8.19030656
    25       2.46058071        0.00013628       0.00017745      -8.19030709
    26       2.46058071        0.00014411       0.00018765      -8.19030714
    27       0.49211614        0.00015118       0.00003937      -8.19030709
    28       0.49211614        0.00008899       0.00002317      -8.19030713
```



Geometry optimization by Newton-type methods

By Taylor-expanding, we have

$$E = E_0 + \sum_i^{3N} \left(\frac{\partial E}{\partial x_i}\right)_0 (x_i - x_i^{(0)}) + \frac{1}{2}\sum_{i,j}^{3N} \left(\frac{\partial^2 E}{\partial x_i \partial x_j}\right)_0 (x_i - x_i^{(0)})(x_j - x_j^{(0)}) + \cdots,$$

The derivative of the total energy w.r.t. coordinates leads to

$$\frac{\partial E}{\partial x_k} = \left(\frac{\partial E}{\partial x_k}\right)_0 + \sum_i^{3N} \left(\frac{\partial^2 E}{\partial x_k \partial x_i}\right)_0 (x_i - x_i^{(0)}).$$

$$\frac{\partial E}{\partial x_k} = 0 \longrightarrow \begin{pmatrix} (\frac{\partial^2 E}{\partial x_1 \partial x_1})_0 & (\frac{\partial^2 E}{\partial x_1 \partial x_2})_0 & \cdots \\ (\frac{\partial^2 E}{\partial x_2 \partial x_1})_0 & (\frac{\partial^2 E}{\partial x_2 \partial x_2})_0 & \cdots \\ \cdots & \cdots & \cdots \end{pmatrix} \begin{pmatrix} (x_1 - x_1^{(0)}) \\ (x_2 - x_2^{(0)}) \\ \cdots \end{pmatrix} = - \begin{pmatrix} \left(\frac{\partial E}{\partial x_1}\right)_0 \\ \left(\frac{\partial E}{\partial x_2}\right)_0 \\ \cdots \end{pmatrix}.$$

$$H\Delta\mathbf{x} = -\mathbf{g},$$

By solving the Eq. for Δx, we have

$$\mathbf{x}^{(n+1)} = \mathbf{x}^{(n)} - (H^{(n)})^{-1}\mathbf{g}^{(n)}.$$

If the Hessian matrix H can be computed, the method is efficient.
However, it may be difficult to evaluate H in general.

Geometry optimization by Newton-type methods

The geometry optimization in OpenMX is based on quasi Newton methods. In Ver. 3.9, the following four methods are available.

$$\mathbf{r}_{\rm new} = \mathbf{r}_{\rm DIIS} + \Delta\mathbf{r} \qquad\qquad \Delta\mathbf{r} = -H^{-1}\mathbf{g}_{\rm DIIS}$$

Methods of calculating approximate Hessian matrix H

DIIS	BFGS	RF(rational function)	EF(eigenvector following)
H=I	BFGS	BFGS+RF	BFGS plus monitoring of eigenvalues of H

Broyden-Fletcher-Goldfarb-Shanno (BFGS) method

$$H_k = H_{k-1} + \frac{|\Delta\mathbf{g}_k\rangle\langle\Delta\mathbf{g}_k|}{\langle\Delta\mathbf{g}_k|\Delta\mathbf{r}_k\rangle} - \frac{|H_k\Delta\mathbf{r}_k\rangle\langle\Delta\mathbf{r}_k H_k|}{\langle\Delta\mathbf{r}_k|H_k|\Delta\mathbf{r}_k\rangle}$$

If the inner product in the red box is positive, the positive definiteness of H is guaranteed.

Approximate initial Hessian by Schlegel

Schlegel proposed a way of constructing an approximate Hessian. A force constant for every pair of elements is fitted to the following formula, where dataset were constructed by B3LYP calculations.

$$F = \frac{A}{(r - B)^3}$$

H.B. Schlegel, Theoret. Chim. Acta (Berl.) 66, 333 (1984); J.M. Wittbrodt and H.B. Schlegel, J. Mol. Struc. (Theochem) 398-399, 55 (1997).

Parameter *B* for Badger's rule computed at the B3LYP level of theory

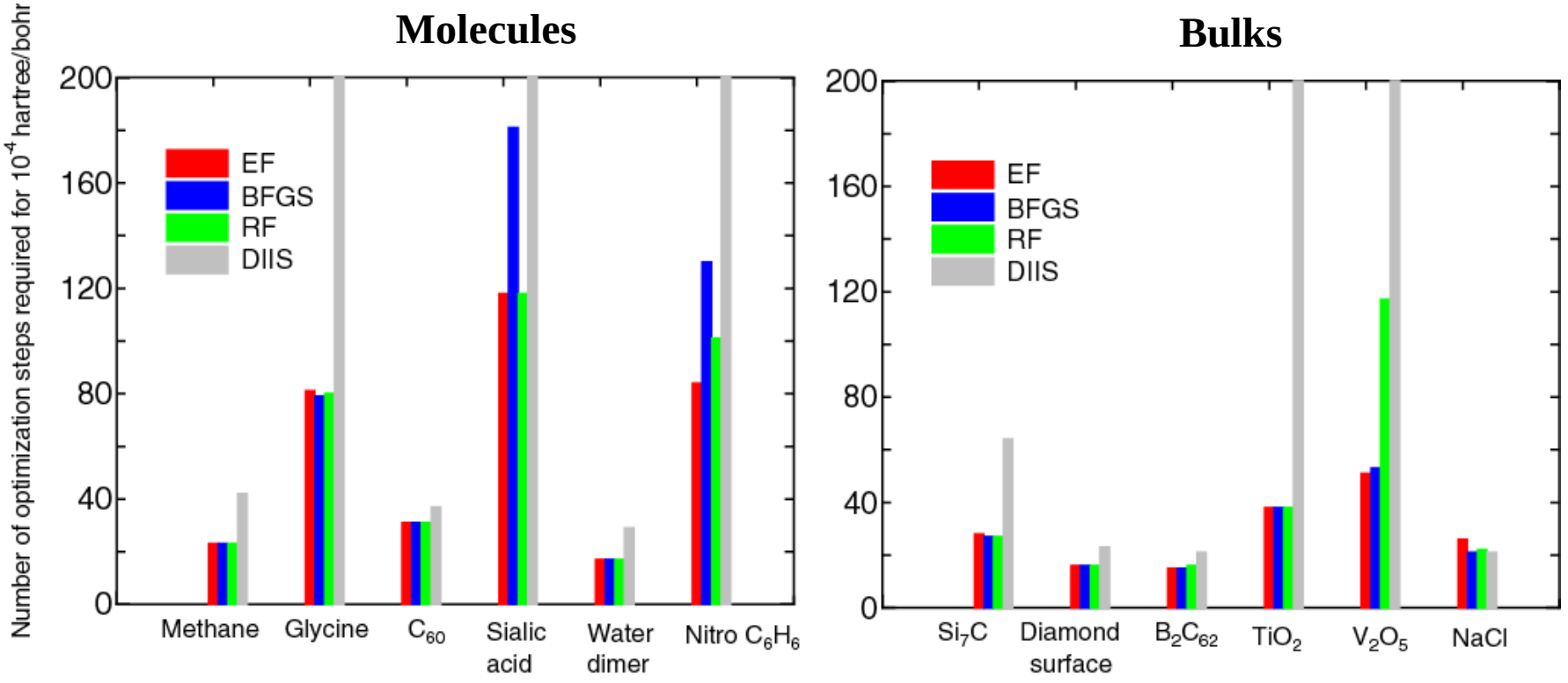
Period	1 H	2 Li–F	3 Na–Cl	4 K–Br	5 Rb–I	6 Cs–At
1	– 0.2573	0.3401	0.6937	0.7126	0.8335	0.9491
2		0.9652	1.2843	1.4725	1.6549	1.7190
3			1.6925	1.8238	2.1164	2.3185
4				2.0203	2.2137	2.5206
5					2.3718	2.5110

Suppose the total energy is given by the sum of pairwise potentials. Then, the derivatives lead to the following relation:

$$V_2 = \frac{1}{2}\sum_i \left(\sum_{Rn} \sum_j f(|r_i + R_n - r_j|) \right) \qquad H = BF$$

where B is the B-matrix of Wilson, H is the approximate Hessian in Cartesian coordinate.

Comparison of four methods



- The benchmark calculations imply that the EF and RF work well.
- Large molecules with structural large freedom are hard to get convergence.

The input file and output files for the benchmark calculations are available in openmx3.9/work/geoopt_example".

Keywords relevant to geometry optimization

```
MD.Type                 EF      # Opt|DIIS|BFGS|RF|EF
MD.Opt.DIIS.History      3      # default=3
MD.Opt.StartDIIS         5      # default=5
MD.Opt.EveryDIIS       200      # default=200
MD.maxIter             100      # default=1
MD.Opt.criterion       1.0e-4   # default=0.0003 (Hartree/Bohr)
```

The behavior of the quasi Newton methods can be controlled by the following two keywords:

```
MD.Opt.DIIS.History     3 # default=3
MD.Opt.StartDIIS        5 # default=5
```

The keyword 'MD.Opt.DIIS.History' gives the number of previous steps to estimate the optimized structure used in the geometry optimization by 'DIIS', 'EF', and 'RF'. The default value is 3.

The geometry optimization step at which 'DIIS', 'EF', or 'RF' starts is specified by the keyword 'MD.Opt.StartDIIS'. The geometry optimization steps before starting the DIIS-type method is performed by the steepest decent method. The default value is 5.

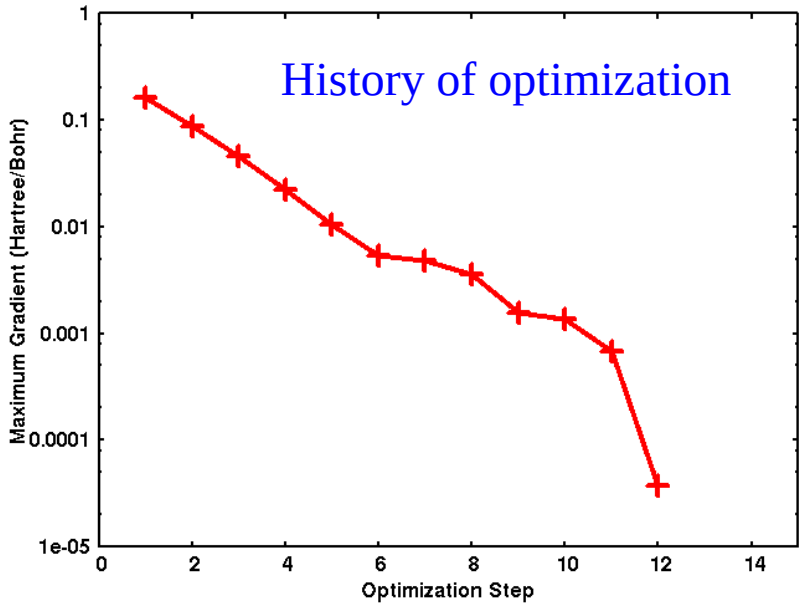
Variable cell optimization

Let us start optimization of diamond lattice with a displacement as

```
Atoms.Number          2
Atoms.SpeciesAndCoordinates.Unit   frac # Ang|AU
<Atoms.SpeciesAndCoordinates
   1     C     0.10000000000000    0.00000000000000   -0.05000000000000      2.0      2.0
   2     C     0.25000000000000    0.25000000000000    0.25000000000000      2.0      2.0
Atoms.SpeciesAndCoordinates>
Atoms.UnitVectors.Unit              Ang # Ang|AU
<Atoms.UnitVectors
  1.6400  1.6400  0.0000
  1.6400  0.0000  1.6400
  0.0000  1.6400  1.6400
Atoms.UnitVectors>
```

Relevant keywords:

```
MD.Type                          RFC5
MD.Opt.DIIS.History               3
MD.Opt.StartDIIS                  7
MD.Opt.EveryDIIS                  100000
MD.maxIter                        100
MD.TimeStep                      1.0
MD.Opt.criterion                0.0003
```

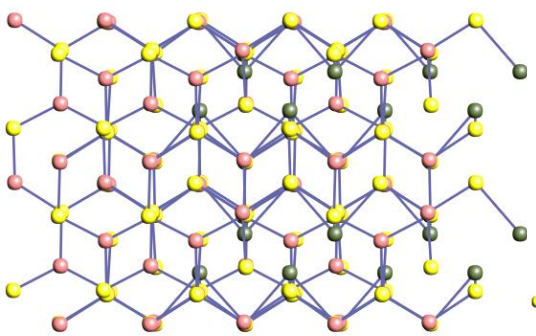


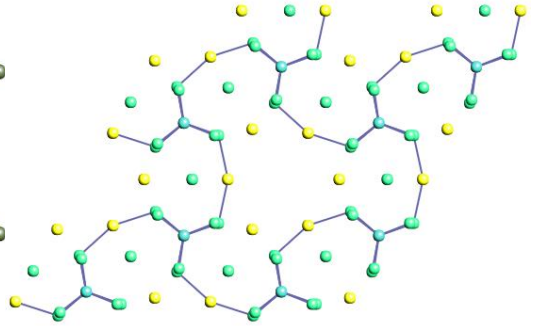
The calculation can be traced by “Cdia-RF5.dat” in work/cellopt_example.

Please see also the page 74 in the manual.

Benchmark calculations of RFC5

For 785 crystals (mostly sulfides) , the full optimization by RFC5 were performed by Mr. Miyata, Ph.D student in JAIST, as computational screening in searching good thermoelectric materials





The optimization criterion: 10^{-4} Hartree/bohr

The histogram shows the number of systems among 785 systems as a function of the number of iterations to achieve the convergence

Restarting of calculations

- After finishing your first calculation or achieving the self consistency, you may want to continue the calculation or to calculate density of states, band dispersion, molecular orbitals, and etc. using the self consistent charge in order to save the computational time. To do this, a keyword 'scf.restart' is available.

```
scf.restart          on        # on|off,default=off
```

- If the first trial for geometry optimization does not reach a convergent result or molecular a dynamics simulation is terminated due to a wall time, one can restart the geometry optimization using an input file 'System.Name.dat#' which is generated at every step for the restart calculation with the final structure.

See also the page 67 in the manual.

Output of large-sized files in binary mode

Large-scale calculations produce large-sized files in text mode such as cube files. The IO access to output such files can be very time consuming in machines of which IO access is not fast. In such a case, it is better to output those large-sized files in binary mode. The procedure is supported by the following keyword:

```
OutData.bin.flag    on    # default=off, on|off
```

Then, all large-sized files will be output in binary mode. The default is 'off'. The output binary files are converted using a small code 'bin2txt.c' stored in the directory 'source' which can be compiled as

```
gcc bin2txt.c -lm -o bin2txt
```

As a post processing, you will be able to convert as

```
./bin2txt *.bin
```

The functionality will be useful for machines of which IO access is not fast.

See also the page 320 in the manual.